[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, THE HEBREW UNIVERSITY]

Some Catalytic Hydrogen Exchange Reactions of Hydrocarbons

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The catalytic exchange reaction of hydrocarbons with molecular hydrogen has been the subject of a large number of investigations.[1b–8] Two different mechanisms have been proposed for the reaction: (a) the dissociative and (b) the associative mechanism. The dissociative mechanism may be formulated as

$$\mathrm{RH_2} \xrightarrow[-\mathrm{H}]{+\mathrm{K}} \mathrm{RH - K} \xrightarrow[+\mathrm{D}]{-\mathrm{K}} \mathrm{RHD} \qquad (1)$$

On the other hand Polanyi and Horiuti have suggested the following associative mechanism for the exchange reaction

$$\mathrm{RH_2} \xrightarrow[+\mathrm{D}]{+\mathrm{K}} \mathrm{RH_2D - K} \xrightarrow[-\mathrm{H}]{-\mathrm{K}} \mathrm{RHD} \qquad (2)$$

(K = catalyst)

The half-hydrogenated compound which is formed by the first step in (2) is according to these authors responsible for the connection between the hydrogenation and exchange reaction, since it is an intermediate compound for both processes.

While all experiments on the exchange of saturated hydrocarbons indicate that in these cases the dissociative mechanism is operative[4,5,9,10] the exact mechanism of the exchange reactions of unsaturated hydrocarbons has not yet been definitely settled.

The present paper reports some results on the exchange of the following pairs of compounds: ethylene and water, *n*-butene and water, *n*-butane and water, *n*-butene and ethylene, and *n*-butane and ethylene. The mechanism of the catalytic exchange reactions is discussed in the light of these findings.

Experimental

Material

Ethylene was obtained either from a cylinder from the Ohio Chemical Co. or by dehydration of ethyl alcohol in the presence of alumina at 400°.

***n*-Butene** was prepared by the dehydration of *n*-butyl alcohol by means of alumina at 400°. The two isomers butene-1 and butene-2 thus obtained were used without separation.

***n*-Butane** was prepared by the hydrogenation of *n*-butene with an excess of hydrogen on a nickel or palladium catalyst.

Heavy *n*-butane was prepared by hydrogenating *n*-butene with deuterium in the presence of either nickel or palladium.

All the above mentioned hydrocarbons were purified by fractional distillation under low pressure.

Palladium Catalyst.—This was prepared by passing hydrogen through a suspension of 5 g. of activated charcoal (lumps) in a concentrated solution of 1 g. of palladium chloride at 50–60° until the solution was completely decolorized. The lumps of catalyst were washed with distilled water, neutralized with a dilute solution of sodium hydroxide, and again washed with distilled water until free of chloride ions. The catalyst was then dried at 100° in vacuum. The catalyst thus obtained contained about 10% palladium by weight.

Nickel Catalyst.—Raney nickel in the form of either powder or lumps was used. It was prepared in the usual way by dissolving out the aluminum with a concentrated solution of sodium hydroxide. The catalyst was protected from contact with air prior to use (for method of handling, see below).

Apparatus and Procedure

Two methods were used: (1) a static method in which the apparatus consisted essentially of a large reaction bulb, and (2) a circulating method in which the reacting gases were circulated over the catalyst by means of a pump.

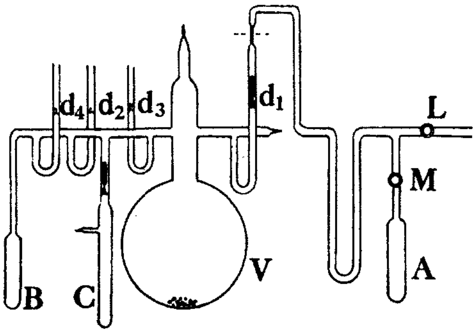

Fig. 1.—Reaction vessel (static method).

(1) In the static method (Fig. 1) reaction vessels 1 to 5 l. capacity were used. They were fitted with one or more break-seals, *d*, for the introduction or withdrawal of samples. The side-arm, B, served for the condensation of the reactants. If water was one of the reactants, it was previously degassed in a small glass tube and sealed off under vacuum. This tube, C, was connected to the reaction vessel via a break-seal. The palladium catalyst was introduced directly into the reaction vessel. When a nickel catalyst was used the following procedure was adopted: the nickel powder or lumps were washed by decantation with distilled water until free of alkali and transferred, while still wet, to a thin-walled glass tube. This tube was then connected via a trap cooled in an acetone–Dry Ice slush to a high vacuum system and the water distilled off. The catalyst was then degassed by heating to 200° for several hours, sealed off, and introduced carefully into the reaction vessel which was then evacuated. Grease and mercury vapors were excluded during this operation by a Dry Ice trap. Known amounts of the gaseous reactants were then distilled into the side-arm, B, by cooling it with liquid air, and the reaction vessel was sealed off. Water, if one of the reactants,

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[1b] A. Farkas, L. Farkas and E. K. Rideal, *Proc. Roy. Soc.* (*London*), **A146**, 630 (1934).

[2] A. Farkas and L. Farkas, THIS JOURNAL, **60**, 22 (1938).

[3] I. Horiuti and M. Polanyi, *Trans. Far. Soc.*, **30**, 1164 (1934).

[4] K. Morikawa, W. S. Benedict and H. S. Taylor, THIS JOURNAL, **58**, 1145 (1936).

[5] K. Morikawa, N. R. Trenner and H. S. Taylor, *ibid.*, **59**, 1103 (1937).

[6] A. Farkas and L. Farkas, *Trans. Far. Soc.*, **33**, 827 (1937).

[7] G. H. Twigg and E. K. Rideal, *Proc. Roy. Soc.* (*London*), **171**, 55 (1939).

[8] G. K. Conn and G. H. Twigg, *ibid.*, **171**, 70 (1939).

[9] A. Farkas and L. Farkas, *Trans. Far. Soc.*, **35**, 917 (1929).

[10] A. Farkas, *ibid.*, **36**, 522 (1940).

was then admitted into the reaction vessel by breaking the appropriate break-seal. If nickel was used as a catalyst, the reaction vessel was shaken vigorously at this stage, until the thin-walled tube containing the catalyst was broken. The reaction vessel was then heated in an electric furnace at a constant temperature for a definite time, after which it was connected through one of its break-seals to the evacuating system, thus enabling a sample of the contents to be withdrawn into A and analysed.

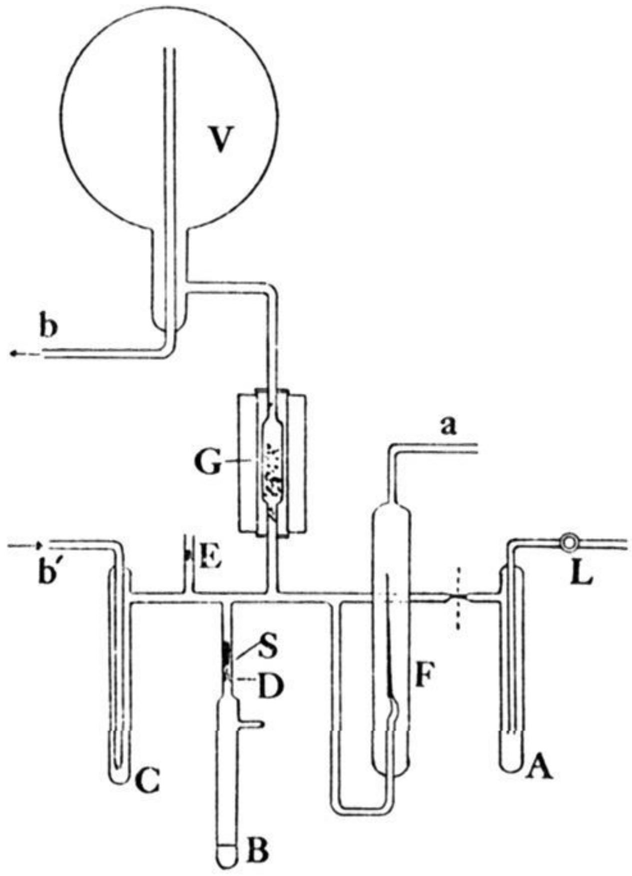

Fig. 2.—Reaction apparatus (circulating method).

(2) In the circulating method (Fig. 2) an all glass electromagnetic pump was used for circulating the reactants over a palladium catalyst heated to the desired temperature in an electric furnace, G. At the start of an experiment, the reaction system was evacuated and the catalyst outgassed at 150°. The reacting gas was then introduced through a trap, A, cooled in an acetone-Dry Ice slush into the tube, C, which was cooled in liquid air. After sealing off from the evacuating system, the break-seal D was broken, so that the water in B distilled over into C; the circulating pump was then started. The temperature of the catalyst was fixed at the desired value and the gas allowed to evaporate and bubble through the water in C which was kept at a constant temperature. After a certain time the reacting gas and water were withdrawn through the break-seal E and analysed. An all glass Bourdon type gage, F, was used to measure the change of pressure in the apparatus.

The electromagnetic pump (Fig. 3) differed in the following details from those described previously.[11,12] (a) Only one electromagnet E was used for lifting the piston (consisting of an iron rod 25 mm. in diameter and 300 mm. long enclosed in a glass tube) and (b) a mercury switch M instead of an electric motor was used for interrupting the current. The pump works as follows: when a direct current from a 220 v. source is switched on, the electromagnet E lifts the piston; at the same time two small electromagnets, D, connected in parallel with E work against the spring, L, and tip the mercury switch, M, so that the current is interrupted. The piston then falls down freely while the spring L brings the switch M back to its initial position. The cycle is then repeated. With a current of 0.3 ampere the pump could circulate 1.1 l., of gas per minute against a back pressure of 110 mm. When only gaseous reactants were used the pump could work for several hundred hours without interruption. When water vapors were circulated, the piston stuck to the glass wall after about fifty hours and had to be cleaned.

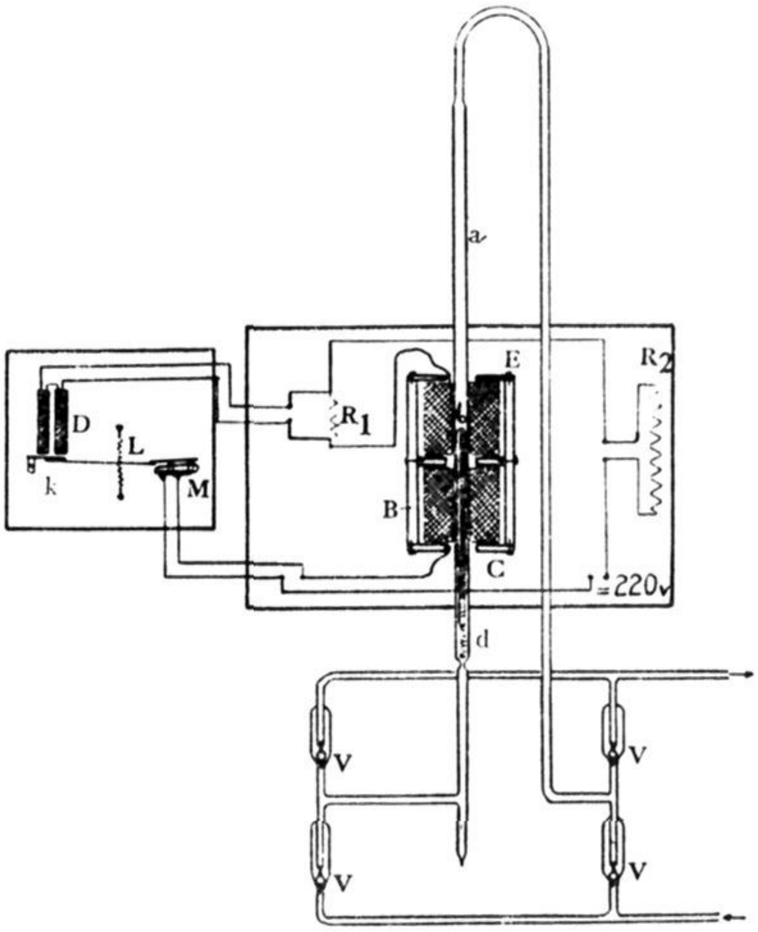

Fig. 3.—All glass electromagnetic circulating pump.

Analytical

The water was separated from the hydrocarbon by distillation in vacuum. It was further purified by the addition of anhydrous sodium carbonate and potassium permanganate and redistilling in vacuum. It was then analyzed for its deuterium content by the float method with an accuracy of 1 part of D_2O in 5 × 10^4 parts of H_2O. If 0.5 to 1 g. of the hydrocarbon were available, it was burnt over platinized asbestos and the water obtained after purification was analyzed by the float method. If only small samples of the hydrocarbon (3–5 mg.) were available, the analysis was carried out by a method described previously[13] consisting of burning the hydrocarbon to water over copper oxide and bringing this water into equilibrium with a minute amount of hydrogen by means of a glowing platinum filament. The deuterium content of the hydrogen was then analyzed by the microconductivity method.

Experimental Results

Exchange between Ethylene and Water.—The results of these experiments are given in Table I. Experiments 1, 2, 3, 15 and 16 were performed by the circulating method, and 4 and 5 by the static method. In Expt. 16 both the water and the ethylene were analyzed, in the others the deuterium content of the ethylene was calculated from the change in the deuterium content of the water. The last column of Table I shows the values of the partition

$$K = (D/H)\text{ ethylene}/(D/H)\text{ water}$$

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[11] R. Livingstone, *J. Phys. Chem.*, **33**, 955 (1929).

[12] W. Brenschende, *Z. physik. Chem.*, **A178**, 74 (1937).

[13] A. Farkas, *Trans. Far. Soc.*, **32**, 413 (1936).

TABLE I

EXCHANGE BETWEEN ETHYLENE AND WATER

				Water				Ethylene				
Expt.	Catalyst	Temp., °C.	Reac. time, hours	Moles	Partial pressure, mm.	% D-content initial	% D-content final	Moles	Partial pressure, mm.	% D-content initial	% D-content final	Partition, K
15	Pd (0.5 g.)	110	190	0.047	300	9.8	9.6	...	...	..	..	..
3	Pd (2 g.)	80	30	.10	17.5	1.00	0.99	0.076	500	0.00	0.00	0.00
1	Pd (2 g.)	120	20	.11	17.5	1.22	1.21	.069	400	.00	.00	.00
16	Pd (1 g.)	110	45	.31	17.5	9.9	9.5	.090	600	.00	.11	.01
2	Pd (2 g.)	170	21	.11	17.5	1.24	1.14	.070	500	.00	.07	.06
4	Pd (1.5 g.)	110	118	.083	350	1.05	0.44	.062	260	.00	.41	.93
5	Ni (5 g.)	110	140	.083	350	4.43	1.69	.088	370	.00	1.29	.76

It is seen from Table I that no exchange, or at most only a very slow one, occurred when the circulating method was used, even at a temperature of 170°. On the other hand, equilibrium was almost reached in the static method experiments. The longer reaction time in Expts. 4 and 5 cannot explain the higher deuterium values observed in the ethylene, and we have to assume that the much higher partial pressure of water (350 mm.) as compared with that in the circulating method experiments (17.5 mm.) is responsible for the higher rate of exchange. The dependence of the rate of exchange on the partial pressure of water and ethylene has not yet been investigated further.

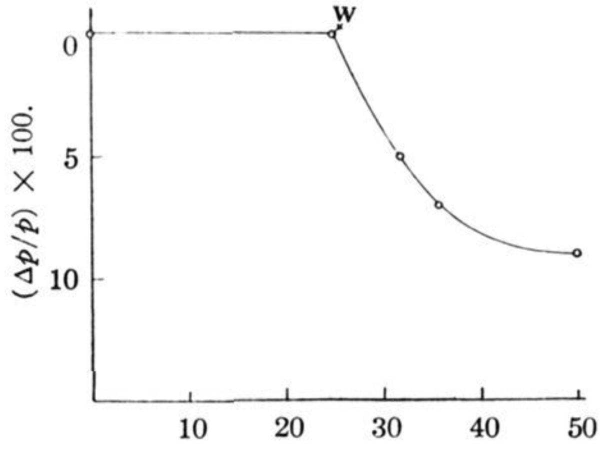

Fig. 4.—Polymerization of ethylene in the presence of water.

It was noticed that, in those experiments in which there was no appreciable exchange, a decrease of the pressure in the reaction system occurred due to polymerization. In Fig. 4 the change of pressure in Expt. 16 is given. It will be seen that the pressure change occurred only in the presence of water but not in the absence of water during the first twenty-five hours. After a certain reaction time, the catalyst becomes poisoned by traces of a high polymer and its activity considerably reduced. By determining the vapor pressure of the polymerization product at eight different temperatures between −60 and −25°, it was found to be butene-2. In Expts. 4 and 5 with high partial pressure of water no polymerization was observed. Besides the polymerization two side reactions also occurred in the presence of the palladium catalyst: the formation of small amounts of ethyl alcohol and acetic acid.

Exchange between Butene and Water.—The experimental results are given in Table II. In Column 13 the equilibrium values of the deuterium content of the butene are given. They were calculated on the assumption that all the eight hydrogen atoms are exchangeable and that the partition coefficient for this reaction is 0.8 (*i. e.*, the same as in the case of the ethylene and water). Column 14 gives the first order velocity constant

$$k = \frac{1}{t} \ln \frac{D_e}{D_e - D_t}$$

where D_e and D_t denote the deuterium content at equilibrium and at time t, respectively. It can be seen that in all cases an exchange between the hydrogen atoms of the water and the hydrogen atoms of the butene took place. Figure 5 shows the course of the exchange in Expt. 21. It can be seen that here also the catalyst gradually lost its activity.

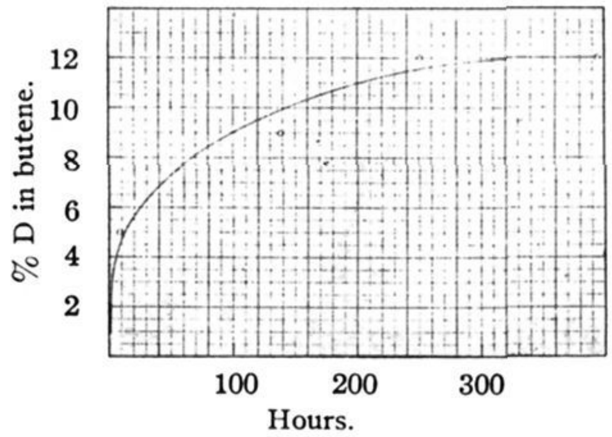

Fig. 5.—Exchange between butene and water at 120°.

The water recovered after exchange in the presence of the palladium catalyst contained an unidentified acid and also a solid polymer which remained behind on evaporating off the water.

Exchange between Butane and Water.—No exchange between butane and water was observed under conditions under which the exchange between butene and water took place readily (catalyst: 2 g. palladium; temperature, 120°; reaction time, 160 hours; p_{H_2O} = 220 mm.; $p_{C_4H_{10}}$ = 20 mm.). This negative result was not due to (accidental) inactivity of the catalyst, since the same catalyst was used in a subsequent experiment (Expt. 20, Table II) for the reaction between butene and water in which an exchange was observed.

TABLE II

EXCHANGE BETWEEN BUTENE AND WATER

				Water				Butene					
Expt.	Catalyst	Temp., °C.	Reacn. time, hours	Moles	Partial pressure, mm.	% D-content initial D_0	% D-content final D_t	Moles	Partial pressure, mm.	% D-content initial D_0	% D-content final D_t	D-content of butene at equilib. %	$k \times 10^3$/hr.
7	Ni (8 g.)	110	166	0.08	320	4.43	1.43	0.09	360	0.0	0.68	0.77	13.2
9[a]	Pd (2 g.)	110	159	.073	280	96.0	53.3	.016	61	0.0	23.8	47.3	4.4
11	Pd (2 g.)	110	235	.058	230	96.0	66.0	.021	83	0.0	21.0	36.3	3.7
12	Pd (2 g.)	110	284	.056	220	96.0	80.2	.018	70	21.0	32.6	51.9	1.7
13	Pd (1 g.)	110	307	.054	200	96.0	85.0	.016	59	32.6	40.2	59.4	1.1
14	Pd (0.5 g.)	110	314	.061	240	96.0	85.0	.0046	18	0.0	21.5	70.4	1.2
20	Pd (0.5 g.)	120	17.5	.058	230	99.6		.0054	21	0.0	3	65.5	2.6
20a	Pd (0.5 g.)	120	61	.058	230	99.6		.0054	21	0.0	8	65.5	2.1
21	Pd (0.5 g.)	120	7.75	.058	230	99.6		.0057	23	0.0	5	68	9.3

[a] In Experiments 9, 13 and 14 the increase of the D-content of butene does not quite correspond to the decrease of the D-content of the water.

TABLE III

EXCHANGE BETWEEN BUTENE AND ETHYLENE

				Ethylene				Butene					
Expt.	Catalyst	Temp., °C.	Reacn. time, hours	Moles	Partial pressure, mm.	% D-content initial D_0	% D-content final D_t	Moles	Partial pressure, mm.	% D-content initial D_0	% D-content final D_t	% D-content at equilib.	$k \times 10^3$/hr.
6	Ni (5 g.)	110	140	0.058	220	1.29	0.77	0.045	170	0	0.34	0.50	
8	Ni (6 g.)	110	211	.061	175	0	0.21	.047	135	0.68	0.54	0.41	3.4
10	Pd (2 g.)	110	123	.0052	125	0	5.5	.0067	150	23.8	21.7	17.1	3.2
17	Pd (0.5 g.)	110	300	.0047	100	0	17	.0116	250	40.2	36.7	33.5	2.4
18	Pd (0.5 g.)	120	10.75	.0011	25	0	7	.0026	60	36	30.4	29.6	25
23	Pd (0.5 g.)	120	90	.0030	70	0	5	.0047	12	12	11.0	9.1	6.3

Exchange between Butene and Ethylene.—The results are given in Table III. In all these experiments, except in Expt. 6, "heavy" butene was used in order to exclude the possibility of an apparent exchange reaction due to dimerization of "heavy" ethylene. Column 13 gives the equilibrium values of the deuterium content of the two hydrocarbons assuming a partition coefficient of 1. All the hydrogen atoms in the butene were assumed to be exchangeable. Column 14 gives the first order velocity constant. In all cases only the deuterium content of the ethylene was determined. Ethylene was chosen rather than butene, since the change in its deuterium content is relatively higher. In Expt. 18, a series of measurements on the progress of the exchange reaction was also made (see Fig. 6). During the reaction no change of pressure occurred.

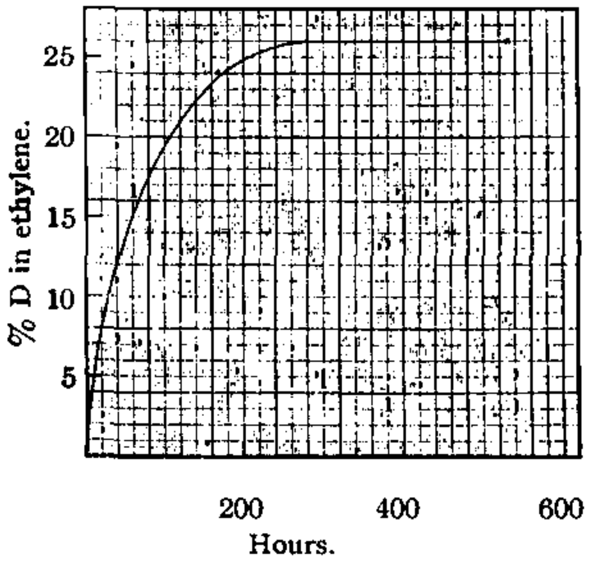

Fig. 6.—Exchange between butene and ethylene.

Exchange between Butane and Ethylene.—The exchange between butane and ethylene was tested by the same procedure as used in Expt. 18 of Table III: 0.0052 mole of butane (D-content 45%) and 0.0021 mole of "light" ethylene were allowed to interact on the palladium catalyst for one-hundred fifteen hours at 120°. After this treatment the deuterium content of the ethylene was found to be 1%. This increase was within the limits of experimental error. After this period, a small amount of "light" butene (0.0002 mole) was introduced into the reaction vessel in order to test whether the exchange between butane and ethylene proceeds via butene. After a period of one-hundred thirteen hours, the deuterium content of the ethylene rose to 1.5%. The possibility that these negative results were due to an accidental inactivation of the catalyst was excluded by using the same catalyst for the exchange of butene and ethylene in Expt. 23 of Table III.

The activity of the same catalyst was also tested for the exchange reaction of butane with deuterium. The catalyst which was used in the butane–ethylene exchange (one-hundred fifteen hours), butane–ethylene–butene exchange (one-hundred thirteen hours) and butene-ethylene (ninety hours; Expt. 23) was brought into contact with 0.0043 mole of "light" butane and 0.0028 mole of deuterium (99.6% D_2) in the same reaction vessel at 120°. The deuterium content in the butane was found to be 6 and 9% after thirteen and one-half and thirty-five and one-half hours, respectively.

Discussion

The exchange of water with ethylene has been observed by Horiuti and Polanyi,[3] and the present experiments are in qualitative agreement with their results. In the experiments of these authors, the ratio $p_{H_2O}/p_{C_2H_4}$ was 2.6. In the present experiments this ratio was about 1 when the static method was used and only 0.029 to 0.044 in the circulating method. These experiments show a strong dependence of the rate of exchange on the ratio of the partial pressures of water and ethylene and the simplest assumption is that water is displaced from the surface of the catalyst by ethylene if the ratio $p_{H_2O}/p_{C_2H_4}$ is low. On the other hand, the absence of dimerization of ethylene in the presence of a high partial pressure of water would suggest that under these conditions the ethylene concentration on the surface layer is low, so that ethylene–ethylene interaction becomes slow. At low partial pressures of water, the dimerization of ethylene could be explained by the well-known mechanism of carbonium ion formation

$$C_2H_4 + H_2O \longrightarrow C_2H_5^+ + OH^- \quad (3)$$

$$C_2H_5^+ + C_2H_4 \longrightarrow C_4H_8 + H^+ \quad (4)$$

If the first step goes only in a forward direction and the second step in this scheme is rapid, it would explain the absence (or relatively slow rate) of exchange of ethylene with water under these conditions. According to this mechanism the deuterium content of the dimer (butene) should have the value of 12.5% (one deuterium atom out of eight hydrogen atoms) if the dimerization were catalyzed by deuterons from pure deuterium oxide. In Expt. 16 of Table I, in which the content decreased from 9.86–9.6% a butene with 1.14% D-content should be obtained. The D-content of the butene formed by dimerization was not determined.

In the case of the exchange reaction between ethylene and water, the possibility that the reaction $C_2H_4 + H_2O \rightleftarrows C_2H_5OH$ contributes substantially to the exchange must be considered. However, a quantitative consideration shows that this is improbable. The equilibrium constant of this reaction is at 110° about 0.068,[14,15] so that at the equilibrium in Expts. 4 and 5 about 1.5% of ethyl alcohol should be formed. In fact only in Expt. 4 in the presence of palladium catalyst was the formation of ethyl alcohol detectable. Nevertheless the exchange also takes place on a nickel catalyst at a similar rate, and in this case there is no evidence that ethyl alcohol is formed.

This observation, together with the fact that ethyl alcohol and water on a platinum catalyst[16] exchange only the hydrogen atom of the hydroxyl group, show that the above reaction is a slow one and does not play an important role in the exchange process under our experimental conditions.

The general features of the butene–water exchange are similar to those of the ethylene–water exchange. In these experiments the $p_{H_2O}/p_{C_4H_8}$ ratio was between 0.9 and 10. These extreme values of the ratio do not influence the rate of exchange to a great extent. On the basis of the present experiments it is not possible to decide whether those hydrogen atoms attached to the double bonded carbon atoms exchange more readily than the remainder. Of particular significance is the absence of exchange between butane and water under conditions under which the exchange between butene and water takes place readily.

Horrex, Greenhalgh and Polanyi[17,18] found that the rate of exchange of benzene with water is about the same as that of cyclohexane and isopentane with water, and inferred that in general the exchange rate of saturated and unsaturated hydrocarbons with water is the same. Our observations indicate that this generalisation is not permissible, and that the similarity in the rates of exchange in the cases investigated by Horrex, Greenhalgh and Polanyi is accidental and dependent upon certain particular experimental conditions (partial pressures and temperature). The experiments on the exchange of ethylene with water show clearly that the ratio of partial pressures has a decisive influence on the rate of exchange of this pair, and it is probable that a more or less pronounced dependence on the ratio of partial pressures of the reactants may also occur in other cases. The comparison of the rate of exchange of butene and butane with water on the same catalyst under identical conditions suggests that in the case of the butane–water pair the absence of exchange is due to a complete displacement of butane by water from the catalyst. This mutual displacement strongly influences the rate of interaction on the catalyst, and it has already been emphasized in previous publications that this effect has to be taken into account.

The same authors also discussed the two possible mechanisms of exchange in the light of their findings that the rate of exchange between water and saturated hydrocarbons was similar to the rate of exchange between hydrogen and saturated hydrocarbons and came to the conclusion that the dissociative mechanism can be operative only if the first step in the scheme

$$RH_4 \underset{-H}{\overset{+K}{\longrightarrow}} RH_3 - K \underset{+H}{\overset{-K}{\longrightarrow}} RH_4$$

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[14] A. W. Francis, *Ind. Eng. Chem.*, **20**, 283 (1928).

[15] A. W. Francis and R. V. Kleinschmidt, *Oil Gas J.*, **27**, 118 (1929).

[16] A. Farkas and L. Farkas, *Trans. Far. Soc.*, **33**, 628 (1937).

[17] C. Horrex, R. K. Greenhalgh and M. Polanyi, *ibid.*, **35**, 511 (1939).

[18] R. K. Greenhalgh and M. Polanyi, *ibid.*, **35**, 520 (1939).

is the rate determining step. It was assumed that the chemisorbed hydrogen atoms on the catalyst arising from the presence of molecular hydrogen must be greater than that arising from the presence of water and therefore the second step should be much faster in the former case than in the latter. Actually we have found this to be the case in our exchange experiments with butane and water and butane and hydrogen so that the above conclusion that the second step cannot be the rate determining step can be upheld in its general form.

The experiments on the exchange of hydrogen atoms between ethylene and butene are of particular interest, in connection with the question as to whether or not unsaturated hydrocarbons undergo dissociation on the surface of the catalyst. Conn and Twigg[8] investigated the interaction of C_2H_4 and C_2D_4 on a nickel catalyst at 76° and 330–360°, but found that no ethylene molecules containing both hydrogen and deuterium atoms were formed, even if the time of interaction was much longer than the half life time of the exchange of ethylene with deuterium on the same catalyst. They considered these experiments as a direct proof that no dissociation of unsaturated compounds takes place to any appreciable extent, and concluded that the exchange of ethylene and deuterium must follow the associative mechanism.

It has been pointed out,[19] however, that this negative result might be due to the fact that under the experimental conditions of these authors the stationary concentration of hydrogen atoms on the surface of the catalyst was so low that the mutual exchange of C_2H_4 with C_2D_4 was inappreciable. The hydrogen concentration on the catalyst might be very low if the atoms formed by dissociation are removed from the catalyst by reaction with ethylene.

The present observations on the exchange of butene with ethylene show directly that unsaturated hydrocarbons can exchange their hydrogen atoms and although the observed rates were not very great (the same order of magnitude as the exchange rates with water) they show that there is only a quantitative difference in the behavior of unsaturated and saturated hydrocarbons. The negative result of the exchange experiment with ethylene and butane is presumably due to the displacement of the butane from the surface of the catalyst by ethylene.

Summary

The following exchange reactions of hydrogen atoms on palladium and nickel catalysts at pressures of 20–700 mm. and in the temperature range of 80–170° were investigated: water and ethylene, water and butene, water and butane, butene and ethylene and butane and ethylene.

It was found that exchange of hydrogen atoms between ethylene and water, butene and water and butene and ethylene does occur while under the same experimental conditions no exchange between butane and water or butane and ethylene was observed.

The experimental results are discussed and the importance of the mutual displacement of the reactants on the catalyst surface is emphasized. The two possible mechanisms for the exchange reactions are discussed in the light of the new experimental evidence.

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[19] A. Farkas, *Trans. Far. Soc.*, **35**, 910 (1939).

[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS]

The Effect of Substituents upon the Rate of Fading of Some Sulfonphthalein Indicators in Alkaline Solutions

BY ELIZABETH E. SAGER, ARTHUR A. MARYOTT AND MARJORIE R. SCHOOLEY

I. Introduction

The usefulness of an indicator in the measurement of *p*H depends, in part, on its chemical stability. Phenolphthalein and some of the substituted phenolphthaleins show a pronounced tendency to fade, particularly in alkaline solutions. Replacement of the carboxyl group in the phenolphthaleins by the sulfonic acid group to form the phenolsulfonphthaleins greatly increases the stability. Sulfonphthaleins covering practically the entire useful *p*H range are available commercially and form one of the most satisfactory series of indicators for colorimetric and spectrophotometric measurements. In the course of a program concerning the application of precise spectrophotometric methods in the determination of ionization constants of indicators, it seemed desirable to examine quantitatively the alkaline stability of a rather complete series. Although the fading rates of certain of the sulfonphthaleins have been the subject of a number of investigations,[1-6] data are lacking in some cases and have been obtained under varied experimental conditions in others, so that an extensive intercomparison of the effect of substituents upon the fading rates cannot be made.

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(1) A. Thiel, *Monatsh.*, **54**, 1008 (1929).

(2) F. W. Panepinto and M. Kilpatrick, THIS JOURNAL, **59**, 1871 (1937).

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